

Energy-Efficient Hexamine Production Process

Anita Kovac Kralj^{*1}

Faculty of Chemistry and Chemical Engineering, University of Maribor
Smetanova 17, Maribor, Slovenia

^{*1}anita.kovac@uni-mb.si

Abstract

Hexamethylenetetramine or hexamine has been known for 100 years as a white chemical compound formed as a product of the reaction between formaldehyde and ammonia. The utilization of hexamine has been widespread but only universally used in small quantities, mainly during the production of explosives, and various resins. Hexamine is produced as a powder or a 42% solution. The aim of this paper was to simulate a more efficient continuous 42% hexamine solution production process in order to operate with minimal cost, and to make full use of exothermic heat flow rate and waste materials.

Keywords

Hexamine; Energy-Efficient Process; Waste Material; Aqueous Solution; Utilities

Introduction

Energy-efficient processes are very important throughout the chemical industry because they can reduce energy losses and costs, and improve the operations of energy and process systems.

Hexamine or hexamethylenetetramine is used in pharmaceutical industries as a primary feed material, and in chemical industries as an intermediate material. It is highly soluble in water and, as with some other tertiary amines, it has an inverse solubility at low temperatures (Smolin & Rapoport, 1959).

The Meissner process is an optimum method to produce hexamine from formaldehyde and gaseous ammonia during which the reaction and crystallization stages take place simultaneously in order to produce crystalline hexamine. The crystallization stage controls the Meissner process due to a high dissolution rate of ammonia and formaldehyde within the aqueous solution and a high reaction rate during hexamine production (Meissner et al. 1954).

The values for those kinetic parameters regarding hexamine crystallization from aqueous solution necessary for controlling industrial crystallizers have been calculated by Alamdari and Tabkhi (Alamdari & Tabkhi, 2004).

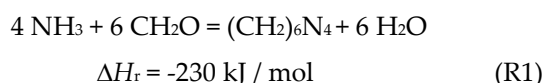
Hexamine, also called hexamethylenetetramine or methenamine (INN), a heterocyclic organic compound that can be prepared by the reaction of formaldehyde and ammonia (Smolin & Rapoport, 1959; Meissner et al., 1954; Zamani et al., 2013; Dan et al., 2011), is crystalline and white in appearance, with the particle sizes ranging from 80-800 micrometers, and moderately soluble in water and very soluble in most organic solvents. It has a cage-like structure similar to adamantane, and holds two very different types of usage: antibiotic (commonly hippurate salt, methenamine hippurate), and solid fuel tablet used for cooking whilst camping. Hexamine is used as a preservative in cheeses under the name of E239. In addition, hexamine can be absorbed through the skin, and some people are allergic to it. This solid fuel in tablet form is used by campers, and military and relief organizations, for heating camping food or military rations, with the characteristic of smoke-free, high energy density, free from liquefaction whilst burning, and no ashes after burning. Another important application for the use of hexamine is in the production of powdery or liquid phenolic resin preparations and phenolic resin moulding compounds, where hexamine is added as a hardening component. These products are used as binders, e.g. in brake and clutch linings, abrasive products, non-woven textiles, those formed parts produced by moulding processes, and fireproof materials (Smolin & Rapoport, 1959; Meissner et al., 1954; Faith et al., 1975).

This paper presents an energy-efficient hexamine production process.

Hexamine Production

Hexamethylenetetramine or hexamine, a heterocyclic organic compound with the formula $(\text{CH}_2)_6\text{N}_4$, was first prepared in 1859 by Butlerov of Russia (Weis et al., 1970). This white crystalline compound is highly soluble in water and polar organic solvents, useful in the synthesis of other chemical compounds, e.g. plastics, pharmaceuticals, rubber additives, and sublimates within a vacuum at 280°C.

Hexamine is produced from ammonia and formaldehyde:



There are mainly two methods in the world to obtain hexamine. In the first, ammonia and formaldehyde are added into the reactor as an aqueous solution, and the second is the use of anhydrous ammonia, if we want to reduce the amount of water entering the reactor. If ammonia is added to a gaseous reactant within a plural relationship of formaldehyde and ammonia at the ratio between 3:2 and 3:3 when the reactor is allowed to be an aqueous solution of formaldehyde, the composition is between $w = 30\text{-}50\%$ formaldehyde. This reaction is exothermic, so the temperature in the reactor is between 50 and 90°C (Gary & Maxwell, 2004) or 102°C (Faith et al., 1975). The ammonia-formaldehyde reaction is highly exothermic. Conversion within the reactor is 97% (Gary & Maxwell, 2004). Passes expire at a pH value between 7 and 8. The reaction mixture is collected in a vacuum evaporator and within it the solution is concentrated until most of the water evaporates, therefore the hexamine is better crystallized. If solid hexamine is required, concentrated aqueous solution is pumped into a crystallizer. The wet crystals are then separated by centrifugation or filtration, and after that, these crystals are washed with water to produce pure hexamine. The crystals are then collected in a spray dryer, as the crystals contain less than 1% water. After drying, the final product is ready for sale (Weis et al., 1979).

This paper presents a more efficient production method to produce continuous 42% hexamine solution.

Continuous 42% Hexamine Solution Production

Hexamine is produced as a granular and free-flowing powder, as well as an approx. 42% solution which is cheaper because it does not need a crystallizer.

Continuous hexamine water solution production is simulated using an Aspen Plus simulator (Aspen Technology, 2004). Firstly, the outlet temperature of the reactor is simulated at 80°C , and then for a second time at 102°C . Continuous hexamine production is produced under a constant pressure of 1 bar. Both simulations are compared.

The purpose of this study was to simulate the production of hexamine solution using an Aspen Plus simulator (Aspen Technology, 2004). This simulator is very common for any engineer assisting in the

planning process. The Aspen Plus simulator calculates the mass flows and energy balances during hexamine production, and analyzes the process at different temperatures by using an ideal thermodynamic model that includes Raoult and Henry equations of state.

Reactor Outlet Temperature of 80°C

The reactor releases 321 kW of heat flow rate (Table 1; Fig. 1). The evaporator was assumed to have a temperature of 101°C , and needed 163 kW of heat flow rate. A temperature of 101°C is the best for the evaporator when producing hexamine which contains 42% aqueous solution. A temperature of 100°C provides 35.0% aqueous hexamine solution but at 102°C this is 50.3% . Table 2 shows the mass flows of the entire process and the composition of the flow simulations at an evaporator temperature of 101°C . The final product (stream 4; 711.1 kg/h), when cooled with water, releases 47 kW of heat flow rate within the cooler.

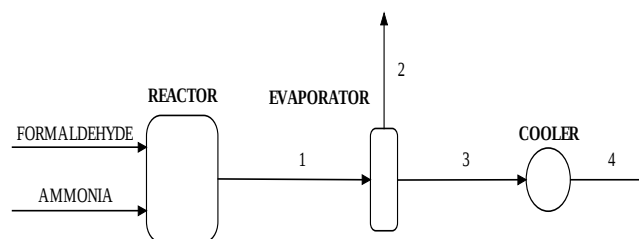


FIG. 1 BASIC SIMULATION PROCESS OF 42% HEXAMINE SOLUTION PRODUCTION

TABLE 1 ENERGETIC STATE OF PROCESS UNITS

Process unit	Φ (kW)
Reactor	-321
Evaporator	163
Cooler	-47

TABLE 2 THE COMPOSITION OF MASS FLOWS SIMULATED DURING THE PRODUCTION OF HEXAMINE WITH A DISCHARGE TEMPERATURE OF 80°C IN THE REACTOR AND 101°C IN THE EVAPORATOR

q_m (kg/h)	AM MO	FOR MA	1	2	3	4
formaldehyde	0.0	400.0	10.6	10.0	0.5	0.5
water	0.0	400.0	633.6	224.7	408.9	408.9
ammonia	151.0	0.0	3.8	3.6	0.1	0.1
hexamine	0.0	0.0	302.9	0.8	302.2	302.2
Temperature, $^\circ\text{C}$	20	20	80	101	101	25
Pressure, bar	1	1	1	1	1	1

Reactor Outlet Temperature of 102°C

The reaction took place at an outlet temperature of 102°C from the reactor, as in the literature (Dan et al., 2011) in which 99 kW heat flow rate (Table 3, Fig. 2)

was released. A partial condenser was analyzed by running at 101 °C, with an entrained heat flow rate of 57 kW, thus producing a 42% aqueous hexamine solution. Table 4 shows the mass flows of the entire process, and the compositions of the flow simulations at a flash temperature of 101 °C. The final product (stream 4; 711.1 kg/h) was cooled within a cooler at a released heat flow rate of 47 kW.

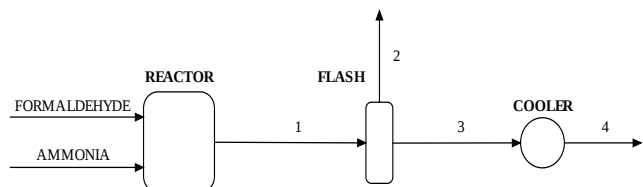


FIG. 2 BASIC SIMULATION PROCESS OF 42% HEXAMINE SOLUTION PRODUCTION

TABLE 3 ENERGETIC STATE OF PROCESS UNITS

Process unit	Φ (kW)
Reactor	-99
Flash	-57
Cooler	-47

It was discovered that an optimum temperature of 101 °C in the flash should be used during the production of hexamine solution in order to remove excess water. The optimal production of hexamine as a 42% aqueous solution, at a reactor outlet temperature of 102 °C, was more energy efficient. The continuous production of hexamine at a high temperature was very simple and effective because this process was disposed at heat flow rate, and did not need flash heating.

TABLE 4 THE COMPOSITION OF MASS FLOW'S SIMULATED PRODUCTION OF HEXAMINE, WITH DISCHARGE TEMPERATURE OF 102 °C FROM THE REACTOR AND 101 °C FROM THE FLASH

q_m (kg/h)	AM MO	FOR MA	1	2	3	4
formaldehyde	0.0	400.0	10.6	10.0	0.5	0.5
water	0.0	400.0	633.6	224.7	408.9	408.9
Ammonia	151.0	0.0	3.8	3.6	0.1	0.1
hexamine	0.0	0.0	302.9	0.7	302.2	302.2
Temperature, °C	20	20	102	101	101	25
Pressure, bar	1	1	1	1	1	1

Energy-Efficient Continuous 42% Hexamine Solution Production

The more beneficial for the production is the one that operates at a maximum temperature (102 °C) because of its totally available heat flow rate, and can be added into the process. Any available heat may be used for the heating of ionized water: firstly within the cooler, followed by within the reactor, and then within the flash. The partly separated water from the flash can be

combined with ionized water, because it contains minimal impurities and this mixed water can be effectively used for hot utilities (Fig. 3).

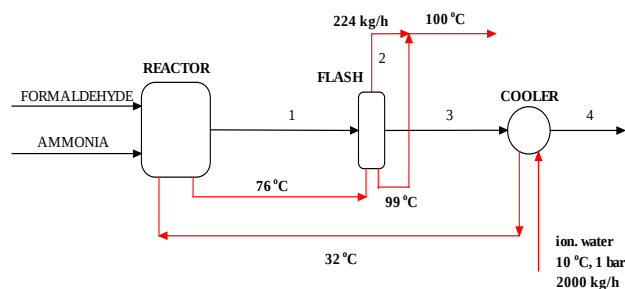


FIG. 3 ENERGY-EFFICIENT SIMULATION PROCESS OF 42% HEXAMINE SOLUTION PRODUCTION

Conclusions

Hexamine has a wide application in the pharmaceutical industries, and in the production of resins. The economic and operational hexamine solution production was more beneficial than the powder production. The most beneficial for the production was the process that operates at a maximum temperature of 102 °C due to the total available heat flow rate, and without the need of heat flow rate. Energy-efficient continuous 42% hexamine solution production is very simple and uses only a small number of processing units. The process itself can heat the hot utilities within all process units separately. No materials are discarded during the process. The water, after separation, could be used as utility or material. However, the aqueous hexamine solution contains a greater volume that is not favorable for transport and storage.

REFERENCES

- Alamdari, A. and Tabkhi, F. "Kinetics of hexamine crystallization in industrial scale." Chem. Eng. and Processing 43, 803 □810, 2004.
- Aspen Technology. ASPEN PLUS User Manual Release 12. Aspen Technology, USA, 2004.
- Faith, W.L., Keyes, D.B., Clark, R.L., Lowenheim, F.A. "Industrial chemicals." W.L. John Wiley & Sons, New York, 1975.
- Gary, R. Maxwell. "Synthetic Nitrogen Products." Kluwer Academic Publishers, New York, 2004. <http://en.wikipedia.org/wiki/hexamine>.
- Liu, Dan, Lei, Jia-Heng, Guo, Li-Ping, Deng, Ke-Jian. "Simple hydrothermal synthesis of ordered mesoporous carbons from resorcinol and hexamine." Carbon 49/6,

- 2113-2119, 2011.
- Meissner, F., Schwiedessen, E. and Othmer, D.F. Shatyski. "Continuous production of hexamethylenetetramine." Ind. Eng. Chem. 46, 724, 1954.
- Smolin, E.M. and Rapoport, L. "The chemistry of heterocyclic compounds, S-Triazines and derivatives." Interscience publication, New York, 1959.
- Weis, Samuel, River, Edge, and Klein, David X. "Continuos process for the product of hexamethylenetetramine." United States Patent Office, 1970.

Anita Kovac Kralj, born on April 26th 1965 in Maribor. Nationality-Slovenian, married with three children. Attended the Technical Faculty in Maribor, finishing in 1989. First employed as a researcher at the Faculty of Chemistry and Chemical Engineering in Maribor. Completed studies for University degree in chemical engineering (1988) while simultaneously employed full-time as assistant and completed Master's thesis at the University of Maribor – Faculty of Chemistry and Chemical Engineering in Maribor (1992). Successfully presented doctorate dissertation in 2002.

Research interest: Process design, retrofit and optimization, energy integration, water reduction, recycling, cleaner production, bio-fuel production, fuel cells .